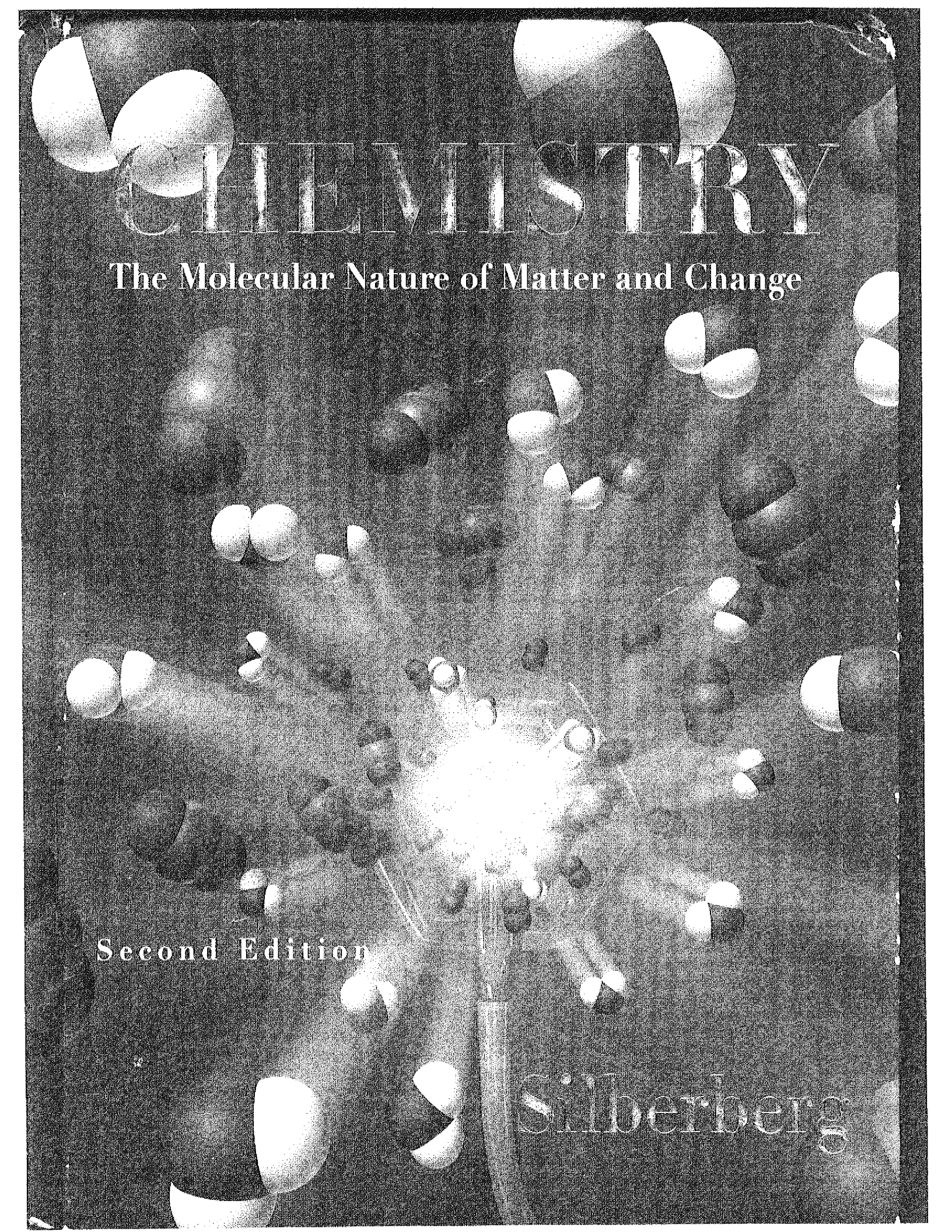


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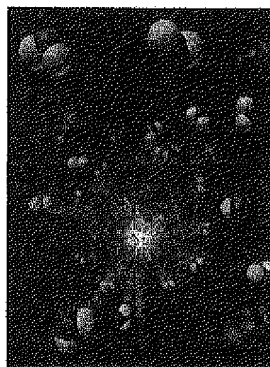


CHEMISTRY

The Molecular Nature of Matter and Change

Second Edition

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CHEMISTRY: THE MOLECULAR NATURE OF MATTER AND CHANGE, SECOND EDITION

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COVER IMAGE: On the molecular level, molecules of methane and oxygen react near the tip of a laboratory burner to form molecules of carbon dioxide and water. As in all chemical change, the number of each type of atom is the same before and after the change: one carbon dioxide and two waters form for every one methane and two oxygens that react.

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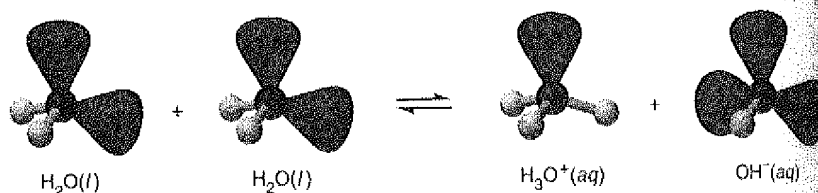
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18.2 Autoionization of Water and the pH Scale

Before we discuss the next major definition of acid-base behavior, let's examine a crucial property of water that enables us to quantify $[\text{H}_3\text{O}^+]$ in an aqueous system: *water is an extremely weak electrolyte*. The electrical conductivity of tap water is due almost entirely to dissolved ions, but even water that has been distilled and deionized repeatedly exhibits a tiny conductance. The reason is that water itself dissociates into ions very slightly in an equilibrium process known as **autoionization** (or self-ionization):



The Equilibrium Nature of Autoionization: The Ion-Product Constant for Water, K_w

Like any equilibrium system, the autoionization of water is described quantitatively by an equilibrium constant:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

Since the concentration of H_2O is essentially constant here, we simplify the equilibrium expression by including the constant $[\text{H}_2\text{O}]^2$ term with the value of K_c to obtain a new equilibrium constant, the **ion-product constant for water**, K_w :

$$K_c[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \quad (18.2)$$

Notice that *one H_3O^+ ion and one OH^- ion appear for each H_2O molecule that dissociates*. Therefore, in pure water, we find that

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M} \quad (\text{at } 25^\circ\text{C})$$

Pure water has a concentration of about 55.5 M (that is, $\frac{1000 \text{ g/L}}{18.02 \text{ g/mol}}$).

these equilibrium concentrations are attained when only one in 555 million water molecules dissociates reversibly into ions!

Autoionization of water has two major consequences for aqueous acid-base chemistry:

1. A change in $[\text{H}_3\text{O}^+]$ causes an inverse change in $[\text{OH}^-]$, and vice versa:

higher $[\text{H}_3\text{O}^+] \Rightarrow$ lower $[\text{OH}^-]$ and higher $[\text{OH}^-] \Rightarrow$ lower $[\text{H}_3\text{O}^+]$

Recall from our discussion of Le Châtelier's principle that a change in concentration of either ion shifts the equilibrium position, but it does *not* change the equilibrium constant. Therefore, if some acid is added, $[\text{H}_3\text{O}^+]$ increases, so $[\text{OH}^-]$ must decrease; if some base is added, $[\text{OH}^-]$ increases, so $[\text{H}_3\text{O}^+]$ must decrease. However, these additions of H_3O^+ or OH^- merely lead to the formation of H_2O , so the value of K_w is maintained.

2. Both ions are present in all aqueous systems. Thus, all acidic solutions contain a low concentration of OH^- ions, and all basic solutions contain a low concentration of H_3O^+ ions. The equilibrium nature of autoionization allows us to define "acidic" and "basic" solutions in terms of relative magnitudes of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$:

In an *acidic* solution, $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

In a *basic* solution, $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

In a *neutral* solution, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

Moreover, if you know the value of K_w at a particular temperature and the concentration of one of these ions, you can easily calculate the concentration of the other ion:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} \quad \text{or} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

Sample Problem 18.2 Calculating $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in Aqueous Solutions

PROBLEM A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[\text{H}_3\text{O}^+] = 3.0 \times 10^{-4} \text{ M}$. Calculate $[\text{OH}^-]$. Is the solution neutral, acidic, or basic?

PLAN We use the known value of K_w at 25°C (1.0×10^{-14}) and the given $[\text{H}_3\text{O}^+]$ to solve for $[\text{OH}^-]$. Then we compare $[\text{H}_3\text{O}^+]$ with $[\text{OH}^-]$ to determine whether the solution is acidic, basic, or neutral. This calculation is very common, so a simple roadmap is shown.

SOLUTION Calculating $[\text{OH}^-]$:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}} = 3.3 \times 10^{-11} \text{ M}$$

Since $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, the solution is acidic.

CHECK It makes sense that adding an acid to water results in an acidic solution. Moreover, since $[\text{H}_3\text{O}^+]$ is greater than 10^{-7} M , $[\text{OH}^-]$ must be less than 10^{-7} M to give a constant K_w .

Follow-up Problem 18.2 Calculate $[\text{H}_3\text{O}^+]$ in a solution at 25°C whose $[\text{OH}^-] = 6.7 \times 10^{-2} \text{ M}$. Is the solution neutral, acidic, or basic?

Expressing the Hydronium Ion Concentration: The pH Scale

In aqueous solutions, $[\text{H}_3\text{O}^+]$ can vary over an enormous range: from about 10 M to 10^{-15} M . To handle numbers with negative exponents more conveniently in calculations, we convert them to positive numbers using a numerical system called a *p-scale*, the negative of the common (base-10) logarithm of the number. ♦ Applying this numerical system to $[\text{H}_3\text{O}^+]$ gives **pH**, the negative logarithm of $[\text{H}^+]$ (or $[\text{H}_3\text{O}^+]$):

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad (18.3)$$

What is the pH of 10^{-12} M H_3O^+ solution?

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 10^{-12} = (-1)(-12) = 12$$

Similarly, a 10^{-3} M H_3O^+ solution has a pH of 3, and a $5.4 \times 10^{-4} \text{ M}$ solution has a pH of 3.27:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = (-1)(\log 5.4 + \log 10^{-4}) = 3.27$$

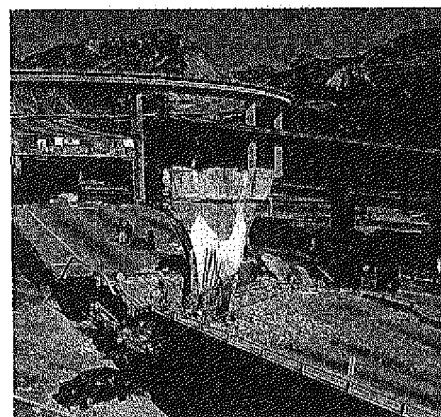
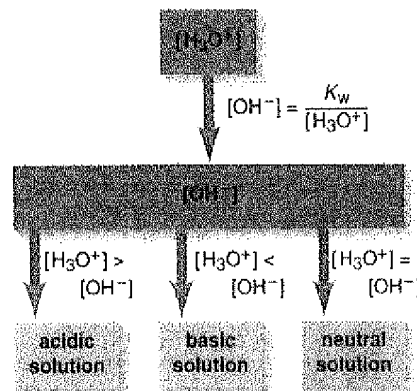
As with any measurement, the number of significant figures in the pH reflects the precision with which the concentration is known. However, since this is a logarithm, recall that the number of significant figures in the concentration equals the number of digits to the right of the decimal point (see Appendix A). In this case, $5.4 \times 10^{-4} \text{ M}$ has two significant figures, so its negative logarithm, 3.27, has two digits to the right of the decimal point.

Note in particular that *the higher the pH, the lower the $[\text{H}_3\text{O}^+]$* . Therefore, *an acidic solution has a lower pH (higher $[\text{H}_3\text{O}^+]$) than a basic solution*. At 25°C in pure water, $[\text{H}_3\text{O}^+]$ is $1.0 \times 10^{-7} \text{ M}$, so

$$\text{pH of a neutral solution} = 7.00$$

$$\text{pH of an acidic solution} < 7.00$$

$$\text{pH of a basic solution} > 7.00$$



♦ Logarithmic Scales in Sound and Seismology

The p-scale is not the only logarithmic scale used in scientific measurements. The decibel scale measures the power of an acoustic signal, and the Richter scale measures the energy of ground movement. Urban planners study noise "pollution" by measuring decibel levels in different city locations at various times of the day. Seismologists record ground movement at stations around the world and try to predict the onset of earthquakes (see photo).

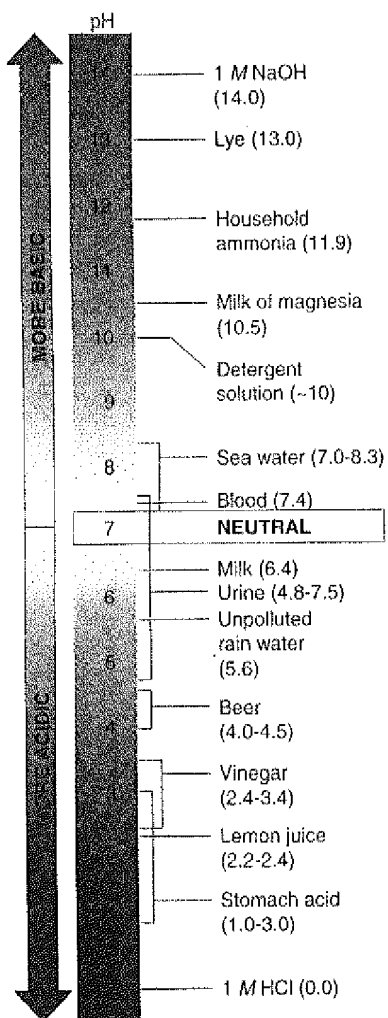


Figure 18.5 The pH values of some familiar aqueous solutions.

Figure 18.5 shows that the pH of some familiar aqueous solutions falls within a range of 0 to 14.

Another important point arises when we compare $[\text{H}_3\text{O}^+]$ in different solutions. Because the pH scale is logarithmic, a solution of pH 1.0 has an $[\text{H}_3\text{O}^+]$ that is 10 times higher than that of a pH 2.0 solution, 100 times higher than that of a pH 3.0 solution, and so forth. To find the $[\text{H}_3\text{O}^+]$ from the pH, you perform the opposite arithmetic process; that is, you find the negative antilog of pH:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

A p-scale is used to express other quantities as well:

- Hydroxide ion concentration can be expressed as pOH:

$$\text{pOH} = -\log [\text{OH}^-]$$

Acidic solutions have a higher pOH (lower $[\text{OH}^-]$) than basic solutions.

- Equilibrium constants can be expressed as pK:

$$\text{pK} = -\log K$$

A low pK corresponds to a high K. A reaction that reaches equilibrium with mostly products (proceeds far to the right) has a low pK (high K), whereas one that has mostly reactants at equilibrium has a high pK (low K). Table 18.3 shows this relationship for some weak acids.

Table 18.3 The Relationship Between K_a and $\text{p}K_a$

Acid Name (Formula)	K_a at 25°C	$\text{p}K_a$
Hydrogen sulfate ion (HSO_4^-)	1.02×10^{-2}	1.991
Nitrous acid (HNO_2)	7.1×10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.0×10^{-10}	10.00

The Relations Among pH, pOH, and $\text{p}K_w$ Taking the negative log of both sides of the K_w expression gives a very useful relationship among $\text{p}K_w$, pH, and pOH:

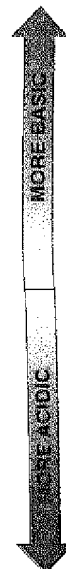
$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \\ -\log K_w &= (-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) = -\log (1.0 \times 10^{-14}) \\ \text{p}K_w &= \text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25^\circ\text{C}) \end{aligned} \quad (18.4)$$

Thus, the sum of pH and pOH is 14.00 in any aqueous solution at 25°C. Since pH, pOH, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$ are interrelated through K_w , knowing any one of the values allows us to determine the others (Figure 18.6).

Sample Problem 18.3 Calculating $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH

PROBLEM In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to 2.0 M, 0.30 M, and 0.0063 M HNO_3 . Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH of the three solutions at 25°C.

PLAN We know from its formula that HNO_3 is a strong acid, so it dissociates completely in water; thus, $[\text{H}_3\text{O}^+] = [\text{HNO}_3]_{\text{init}}$. We use the given concentrations and the value of K_w to calculate $[\text{OH}^-]$ and then use these concentrations to calculate pH and pOH.



	$[\text{H}_3\text{O}^+]$	pH	$[\text{OH}^-]$	pOH
BASIC	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
	1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
	1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
	1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
	1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
NEUTRAL	1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
	1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
	1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
ACIDIC	1.0×10^0	0.00	1.0×10^{-14}	14.00

Figure 18.6 The relations among $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH. Because K_w is constant, $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are interdependent, and change in opposite directions as the acidity or basicity of the aqueous solution increases. The pH and pOH are interdependent in the same way. Note that at 25°C, the product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is 1.0×10^{-14} , and the sum of pH and pOH is 14.00.

SOLUTION Calculating the values for 2.0 M HNO_3 :

$$[\text{H}_3\text{O}^+] = 2.0 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 2.0 = -0.30$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0} = 5.0 \times 10^{-15} \text{ M}$$

$$\text{pOH} = -\log (5.0 \times 10^{-15}) = 14.30$$

Calculating the values for 0.30 M HNO_3 :

$$[\text{H}_3\text{O}^+] = 0.30 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.30 = 0.52$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.30} = 3.3 \times 10^{-14} \text{ M}$$

$$\text{pOH} = -\log (3.3 \times 10^{-14}) = 13.48$$

Calculating the values for 0.0063 M HNO_3 :

$$[\text{H}_3\text{O}^+] = 6.3 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.3 \times 10^{-3}) = 2.20$$

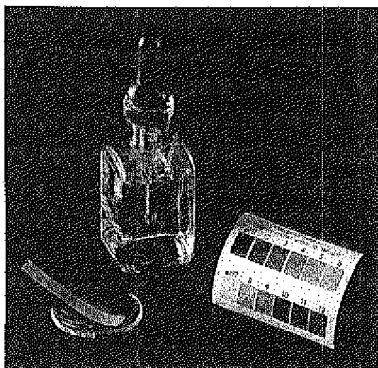
$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-3}} = 1.6 \times 10^{-12} \text{ M}$$

$$\text{pOH} = -\log (1.6 \times 10^{-12}) = 11.80$$

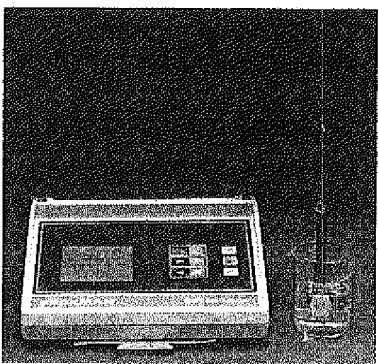
CHECK As the solution becomes more dilute, $[\text{H}_3\text{O}^+]$ decreases, so pH increases, as we expect. Since an $[\text{H}_3\text{O}^+]$ greater than 1.0 M, as in 2.0 M HNO_3 , gives a positive pH, it results in a negative pH. The arithmetic seems correct because $\text{pH} + \text{pOH} = 14.00$ in each case.

COMMENT On most calculators, finding the pH requires several keystrokes. For example, to find the pH of 6.3×10^{-3} M HNO_3 solution, you enter “6.3, EXP, 3, \div , log, +/-”.

Follow-up Problem 18.3 A solution of NaOH has a pH of 9.52. What is its pOH, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$ at 25°C?



A



B

Figure 18.7 Methods for measuring the pH of an aqueous solution. A, A few drops of the solution are placed on a strip of pH paper, and the color is compared with the color chart. B, The electrodes of a pH meter immersed in the test solution measure $[\text{H}_3\text{O}^+]$. (In this equipment, two electrodes are housed in one probe.)

Measuring pH In the laboratory, pH values are usually obtained with an acid-base indicator or, more precisely, with an instrument called a pH meter. **Acid-base indicators** are organic molecules whose colors depend on the acidity or basicity of the solution in which they are dissolved. The pH of a solution is estimated quickly with *pH paper*, a paper strip impregnated with one or a mixture of indicators. A drop of test solution is placed on the paper strip, and the color of the strip is compared with a color chart, as shown in Figure 18.7A.

The *pH meter* measures $[\text{H}_3\text{O}^+]$ by means of two electrodes immersed in the test solution. One electrode provides a stable reference voltage; the other has an extremely thin, conducting, glass membrane that separates a known internal $[\text{H}_3\text{O}^+]$ from the unknown external $[\text{H}_3\text{O}^+]$. The difference in $[\text{H}_3\text{O}^+]$ creates a voltage difference across the membrane, which is measured and displayed in pH units (Figure 18.7B).

Section Summary

Pure water has a low conductivity because it autoionizes to a small extent. This process is described by an equilibrium reaction whose equilibrium constant is the ion-product constant for water, K_w (1.0×10^{-14} at 25°C). Thus, $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are inversely related. In acidic solution, $[\text{H}_3\text{O}^+]$ is greater than $[\text{OH}^-]$, the reverse is true in basic solution, and the two are equal in neutral solution. To express small $[\text{H}_3\text{O}^+]$ values more simply, we use the pH scale ($\text{pH} = -\log [\text{H}_3\text{O}^+]$). A high pH represents a low $[\text{H}_3\text{O}^+]$. Similarly, $\text{pOH} = -\log [\text{OH}^-]$, and $\text{pK} = -\log K$. In acidic solutions, $\text{pH} < 7.00$; in basic solutions, $\text{pH} > 7.00$; and in neutral solutions, $\text{pH} = 7.00$. The sum of pH and pOH equals pK_w (14.00 at 25°C).

18.3 Proton Transfer and the Brønsted-Lowry Acid-Base Definition

Earlier we noted a major shortcoming of the classical (Arrhenius) definition: many substances that yield OH^- ions when they dissolve in water do not contain OH in their formulas. Examples include ammonia, the amines, and many salts of weak acids, such as NaF. Another limitation of the Arrhenius definition was that water had to be the solvent for acid-base reactions. In the early 20th century, J. N. Brønsted and T. M. Lowry suggested definitions that remove these limitations. (Recall that we discussed their ideas briefly in Section 4.2.) According to the **Brønsted-Lowry acid-base definition**,

- An acid is a **proton donor**; any species that donates an H^+ ion. An acid must contain H in its formula; HNO_3 and H_2PO_4^- are two of many examples. All Arrhenius acids are Brønsted-Lowry acids.
- A base is a **proton acceptor**; any species that accepts an H^+ ion. A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3 , CO_3^{2-} , F^- , as well as OH^- . Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^- .

From the Brønsted-Lowry perspective, the only requirement for an acid-base reaction is that *one species donate a proton and another species accept it*; an acid-base reaction is a *proton transfer process*. Acid-base reactions can occur between gases, in nonaqueous solutions, and in heterogeneous mixtures, as well as in aqueous solutions.

An acid and a base always work together in the transfer of a proton. In other words, one species behaves as an acid only if another species *simultaneously* behaves as a base, and vice versa. Even when an acid or a base merely dissolves in water, an acid-base reaction occurs because water acts as the other partner. Consider two typical acidic and basic solutions: